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## CONTENTS

	PAGE
Introduction—Fourth Symposium on Organic Analytical Reagents— JOHN H. YOE.....	277
A Progress Report on Organic Analytical Reagent Studies— W. J. FRIERSON .....	279
Organic Reagents Used in the Determination of Iron— WILLIAM E. TROUT, JR.....	281
A Note on 8-Mercaptoquinoline—J. R. TAYLOR.....	289
Some Substituted Phenolsulfonephthaleins—J. R. TAYLOR, R. S. ROSEN- FELD AND J. W. MARTIN, JR.....	290
Reactivities of Certain Organic Compounds with Inorganic Ions— F. H. FISH, P. J. WALKAUSKAS AND M. FOX.....	292
Progress Report on Inorganic Analysis with Organic Reagents— E. LOUISE WALLACE AND ALFRED R. ARMSTRONG.....	292
Organic Solvents and Wash Liquids in Analytical Chemistry— LONDON ARNDALE SARVER.....	293
<i>Anti</i> -Dianisalacetoneoximehydroxylamine as a New Organic Reagent for the Gravimetric Determination of Tungstates—A. LETCHER JONES AND JOHN H. YOE.....	301
Sodium Catechol Disulfonate as a New Colorimetric Reagent for Iron A. LETCHER JONES AND JOHN H. YOE.....	301
Spectrophotometric Studies of Some Complex Copper Compounds— JAMES W. COLE, M. BROOKS SHREAVES AND JAMES E. BOWDEN....	302
Organic Analytical Reagent Studies: New Colorimetric Reagents for Silver, Copper, Cobalt, Zirconium, and Phenothiazine—JOHN H. YOE AND LYLE G. OVERHOLSER.....	304
Reactivity of Substituted Thioureas—LYLE G. OVERHOLSER AND JOHN H. YOE .....	306

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# *The Virginia Journal of Science*

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Fourth Symposium on Organic Analytical Reagents

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## Introduction

JOHN H. YOE

This afternoon is the fourth anniversary of our symposium which has been held on the occasion of the annual meeting of the Virginia Academy of Science and which has formed a part of the Chemistry Section programs. In spite of increased duties imposed upon various members of our group, incident to the national emergency, it is encouraging to report that very definite progress has been made during the past twelve months. May I take this occasion to express my regret that it has not been possible for me to visit the cooperating institutions during the past year as often as I should have liked; in fact, several have not been visited at all, though I hope to do so within the near future. This failure on my part you will understand I am sure, has not been through a lack of interest but on account of the fact that the major part of my time has been devoted to war work.

To date more than 5000 organic compounds have been investigated by the ten cooperating institutions; about 2700 of these were studied by the group at the University of Virginia; the others were investigated at our sister institutions. The compounds represent a great variety of substances from the standpoint of molecular structure and their study is leading to a better knowledge of the relationships between the structure of organic molecules and their reactivity as analytical reagents. Such studies open the way to the discovery of new specific and highly sensitive organic reagents in inorganic analysis. Today, more than ever before, demands are being made upon the analyst for "trace" analyses. Minute amounts of many constituents that were seldom determined a decade or two ago, are now often de-



terminated with a high degree of accuracy as a matter of routine necessity.

Approximately 250 compounds have been investigated at the University of Virginia during the past twelve months. As in previous years, the reactions observed were mostly the result of oxidation of the organic compounds by ions having relatively high oxidation-reduction potentials, such as  $\text{Ce}^{+4}$ ,  $\text{Au}^{+3}$ ,  $\text{Ir}^{+4}$ ,  $\text{Fe}^{+3}$ , etc. Few of the reactions appear to be valuable in chemical analysis. Two, however, may be mentioned that might find useful applications: Sodium-1,8-dihydroxynaphthalene-3, 6-disulfonate and tetradecylbetaine. The former gives a deep red colored solution with  $\text{Ti}^{+4}$  in acid medium; the latter precipitates gold, platinum and iridium.

Work on 2-thio-5-keto-4-carbethoxy-1, 3-dihydropyrimidine as a silver reagent has been completed. The study of the reactions of substituted thioureas has also been finished. Further work was done on the reactions of 5-chlorobromamine acid with zirconium and on the reaction of 2,4-diacetoxybenzonitril with copper. Spectrophotometric measurements will be made of the latter reaction.

The reaction of phenothiazine with palladous chloride has been studied in considerable detail. The complex formed was isolated and the reaction has been used as a basis for the colorimetric determination of small amounts of phenothiazine.

A spectrophotometric study of the reaction of nitrosoresorcinol with cobalt has been made, including the effect of pH, salt concentration, interfering ions, etc. Procedures have been developed for determining cobalt in the presence of iron and nickel.

We regret that it has not been possible for several of the co-operating institutions to be represented on our program this afternoon. We acknowledge with thanks the contribution to our symposium by Dr. Landon A. Sarver, American Viscose Corporation. Papers and progress reports will now be presented by representatives from: Hampden-Sydney College, Mary Baldwin College, Washington and Lee University, Virginia Polytechnic Institute, College of William and Mary, and the University of Virginia.

UNIVERSITY OF VIRGINIA.

## A Progress Report on Organic Analytical Reagent Studies

W. J. FRIERSON

In 1939 Malowan<sup>1</sup> reported a new method for the detection of gold by the use of morpholine. He reported the test sensitive to 1 part in 50,000 and that copper and iron do not interfere because they are precipitated from the solution by morpholine. The gold first gives a yellow color but this gradually changes to a blue-violet.

Among the organic compounds recently investigated, it was found that 4-amino-3-methylphenyl morpholine,



gives a test for gold which is sensitive to 1 part in 30,000,000. The reagent produces a pink color with gold and reacts with several other ions; chromium, vanadium, osmium and europium, pink color; copper, purple color; platinum, brown precipitate; silver, purple precipitate; and ferric iron, purple color. Silver reacts only in neutral solution; the other ions give best results at pH 3 to 5.

Because this seems to be a promising reagent for the detection and determination of gold, a detailed investigation has been started.

### SOLUBILITY OF THE REAGENT

Solvents examined were water, acetone, alcohol, and several mixtures of alcohol and water. The reagent is only slightly soluble in water, a few milligrams per ml. at 25 C. In acetone, 95% alcohol, 50% alcohol and 25% alcohol the compound is very soluble, giving deep reddish-brown solutions. The solutions seem to be stable, no change being noted on standing several months. A 0.2 per cent solution in 50% alcohol was used for the tests. The standard gold solution contained 0.9 mg. of gold per ml. and more dilute solutions were prepared by dilution.

### EFFECT OF ACIDITY ON THE REAGENT

Tests were made at pH values from 2 to 11 using a solution of gold containing 1 part in 10,000,000. A good color is formed over the pH range 1 to 5, the optimum being pH 2.5 to 3.0. Above pH 7 no satisfactory results were obtained.

## STABILITY OF COLOR

The pink color seems fairly stable when formed from a solution of gold at a concentration of 1 part per million. On standing six days the color fades slightly and takes on a purple hue. In more dilute solutions the color may fade within a few minutes. The stability of the color seems to depend to some extent on the pH of the solution but only a few preliminary tests have been made.

## REFERENCE

1. Malowan, L. S., *Z. anal. Chem.* *118*, 100 (1939).

HAMPDEN-SYDNEY COLLEGE.



## Organic Reagents Used in the Determination of Iron

WILLIAM E. TROUT, JR.

Those of us who have had even a small part in the cooperative research program directed by Professor Yoe will recall the high frequency with which organic compounds produce colors or precipitates with iron. The literature records well over a hundred organic compounds employed in some manner in the determination of iron. The accompanying table indicates the relative distribution of some of these compounds among the classes suggested by Yoe and Sarver in their recent book on *Organic Analytical Reagents* (1). The names and line formulas of the compounds are given and also, for some of the salinogenic reagents, the sensitivities expressed as the ratio of parts of iron to parts of solvent.

Of the solvents listed (I), the first seven have been used to extract and intensify the colored compounds formed in colorimetric analyses. *n*-Amyl alcohol, for example, is thus used in the salicylic acid method for the determination of ferric iron. The last three solvents have been used to extract ferric chloride from its aqueous solutions containing hydrochloric acid.

No attempt has been made to complete the lists of compounds in the first five classes, and no reagents for iron are recorded in Yoe and Sarver's Classes VI, IX, and X.

Our principal interest here is in the salinogenic compounds of Classes VII and VIII.

In the first group of phenolic substances (VII-A-b), at least one hydroxyl is present, and in the compounds listed there is a nearby oxygen atom, either in a hydroxyl group, an ether linkage, or a carbonyl group, through which chelation might take place. In chromotropic acid the hydroxyls are in the 1,8 positions in the naphthalene nucleus.

Not listed here are meta-bromophenol and alpha-naphthol trisulfonic acid, reported by J. R. Taylor (2) at our Symposium last spring. Kojic acid (2-hydroxymethyl-5-hydroxy-1,4-pyrone) has also been proposed as a colorimetric reagent for iron (3). Of special interest in this group is the sodium salt of pyrocatechol-3,5-disulfonic acid, announced last spring as a reagent for iron, about which a further report will be made this afternoon by J. H. Yoe and A. L. Jones.

The second group of compounds (b') presumably from chelate rings in which the hydrogen of the hydroxyl is replaced by the metal ion and the ring is closed through the ring nitrogen. 8-Hydroxyquinoline forms an insoluble ferric compound of this nature which is used in a gravimetric procedure. This precipitate may be centrifuged and dissolved in 95 per cent alcohol, con-

taining a little sodium hydroxide, to form a dark green solution suitable for colormetric determination.

Of these reagents, *ferron*, first used by Yoe, is perhaps the best known to the Symposium group of chemists and needs no further discussion. Snell (4) states that "This reagent has probably been reported in more detail as to possible interference by other ions than any other one". The intense green color is specific for ferric ions, and is very sensitive.

Alloxan and alloxantin may not belong in this class, for, although they contain enolizing groups, there is a possibility that the intense blue compounds formed may result from coordination through two ring nitrogens, as in the 2,2'-dipyridyl complex.

The lake-forming dyestuffs, which are generally used to increase the visibility of small amounts of insoluble hydroxides such as ferric hydroxide, are usually regarded as adsorbed on the hydroxide. It is also probable that these dyes may form salts of the metals.

Acetylacetone enolizes to form a mono- or dihydroxy compound (probably the former) which produces an intense red color with ferric ion suitable for colorimetric analysis.

Dimethyl glyoxime produces a sensitive red color with ferrous compounds that may be used in colorimetry.

Both salicylaldoxime and resorcyalaldoxime may be used in colorimetric analysis.

The well-known cupferron and the corresponding naphthyl compound, neocupferron, precipitate ferric iron from acid solution making possible some otherwise difficult separations.

The relatively long list of isonitroso and related compounds under *i* form intense colors (usually blues) with ferrous ions; some of them are highly sensitive reagents for the detection of iron. Di-isonitrosoacetone forms an intense blue color in aqueous solution. Isonitrosoacetophenone is used in chloroform solution; the chloroform dissolves the blue ferrous complex and intensifies the color, providing a very sensitive test.

Sarver has suggested the use of 2-nitroso-1-naphthol-4-sulfonic acid as a very sensitive colorimetric reagent for iron.

Among the hydroxy-carboxylic acids, salicylic, sulfosalicylic, and beta-resorcylic acids are related compounds which produce colors with ferric ions suitable for colorimetry. Salicylic acid has been used for many years, and has been given considerable study. Protocatechuic acid has been studied recently as a colorimetric reagent for iron (5). Sulfosalicylic acid produces a yellow color with both ferrous and ferric ions in ammoniacal solution and a red color with ferric iron in slightly acid solution, permitting the determination of both ferrous and ferric ion concentrations with the same reagent. Unfortunately, it is necessary to wait four hours for the development of the colors (8, 9, 10).

o-Quinaldic acid, with a carboxyl group ortho to the ring nitrogen of quinoline, produces a red color with ferric ions suitable for use in colorimetry.

The arsonic and sulfinic acids listed in the next groups form insoluble ferric salts suitable for use in gravimetric analysis.

Among the thio compounds, thioglycolic acid (mercaptoacetic acid) has been given careful study as a reagent for use in colorimetry. This acid has been used for the determination of iron in milk, blood, urine, feces, etc. The reagent reduces the ferric blue-purple to the ferrous red-purple, but the ferric color may be restored by shaking in air, even after 24 hours.

The imino compounds listed produce colors with iron.

Alloxan and alloxantin are here classified (VII-C-b) in accordance with the possible functional groups.

The amino compounds of Class VIII form colors, precipitates, or microcrystals with iron, for which analytical applications have been suggested.

Among the nitrogen ring compounds, alloxan, alloxantin, and antipyrine are again classified as previously indicated, because of the possibility of their action with iron through their ring nitrogen atoms.

2,2'-Dipyridyl, 2,2'-phenanthroline, 2-pyridylhydrazine, and the remaining compounds, with the exception of quinoline, produce colors with ferrous iron. Note that each of them contains two nitrogen atoms in different rings.

2,2'-Dipyridyl is a useful reagent for the colorimetric determination of ferrous iron. It is sensitive and specific, with relatively few interfering ions. It has been used to distinguish hematin and non-hematin iron in yeast, and to determine iron in egg-yolk, grains, etc.

2,2'-Phenanthroline and pyramidone have been used as colorimetric reagents for iron.

Excluding the colorimetric methods utilizing thiocyanate, ferrocyanide, ferricyanide, sulfide, and chloride of iron, there are listed in Yoe's *Photometric Chemical Analysis, Vol. I (Colorimetry)* (6), published in 1928, three organic colorimetric reagents for iron; namely, salicylic acid, dimethyl glyoxime, and acetylacetone. Snell and Snell, in *Colorimetric Methods of Analysis* (4), published in 1936, described the use of twelve organic colorimetric reagents for iron. Several have been added to the list during the intervening years. Although some of these reagents have proved their usefulness under proper conditions, much more detailed study appears to be warranted in many cases, and we feel safe in saying that the ideal colorimetric reagent for iron is yet to be found.

Among the great number of organic compounds available or

yet to be synthesized, we may confidently expect to find many more that will be useful in the determination of iron.

An extensive bibliography is not necessary here, since exhaustive references to these compounds may be conveniently obtained from Yoe and Sarver's *Organic Analytical Reagents*. (1).

## Table of Organic Reagents Used in the Determination of Iron

(According to Yoe and Sarver's Classification)

### I. Solvents and Wash Liquids

Carbon disulfide	$\text{CS}_2$
Chloroform	$\text{CHCl}_3$
Carbon tetrachloride	$\text{CCl}_4$
<i>n</i> -Amyl alcohol	$\text{C}_5\text{H}_{11}\text{OH}$
Ethyleneglycol monomethyl ether	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$
Ethyleneglycol mono- <i>n</i> -butyl ether	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OH}$
Ethyl ether	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
Isopropyl ether	$\text{C}_3\text{H}_7\text{OC}_3\text{H}_7$
Dichloroethyl ether	$\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$

### II. Organic Acids and Bases Used in Neutralization and Control of pH

Acetic acid	$\text{CH}_3\text{COOH}$
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$
Succinic acid	$(\text{CH}_2\text{COOH})_2$
Hexamethylenetetramine	$(\text{CH}_2)_6\text{N}_4$

### III. Organic Oxiding Agents

Methylene Blue	$\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$
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### IV. Organic Reducing Agents

<i>p</i> -Phenetidine	$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OC}_2\text{H}_5$
<i>p</i> -Phenylenediamine	$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$
2,5-Bis-(2,4-dimethyl- <i>N</i> -pyrryl)	
3,6-dibromohydroquinone	$\text{C}_6\text{Br}_2(\text{OH})_2(\text{CH}_3\text{C}_4\text{H}_2\text{N}\cdot\text{CH}_3)_2$

### V. Indicators

Alizarin	$\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_2(\text{OH})_2$
Alizarin Red S	$\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}(\text{OH})_2\text{SO}_3\text{H}$



## VII. Acid Salinogenic Compounds

### A. ACIDITY DUE TO ALCOHOLIC HYDROXYL GROUPS

#### *b. Phenolic substances*

Chromotropic acid	$(\text{HO})_2 \cdot \text{C}_{10}\text{H}_4 \cdot (\text{SO}_3\text{H})_2$
2,4-Dihydroxyacetophenone	$\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_3 \cdot (\text{OH})_2$ 1:1,000,000
Gallic acid	$(\text{OH})_3 \cdot \text{C}_6\text{H}_2 \cdot \text{COOH}$
Pyrocatechol	$\text{C}_6\text{H}_4 \cdot (\text{OH})_2$
Pyrocatechol-3,5-disulfonic acid, sodium salt	$(\text{OH})_2 \cdot \text{C}_6\text{H}_2 \cdot (\text{SO}_3\text{Na})_2$ 1:75,000,000
Pyrogallol	$\text{C}_6\text{H}_3 \cdot (\text{OH})_3$
Pyrogallol dimethyl ether	$(\text{OH}) \cdot \text{C}_6\text{H}_3 \cdot (\text{OCH}_3)_2$

#### *b'. Phenolic hydroxyl and nitrogen ring*

Alloxan	$\text{CO} : (\text{NH} \cdot \text{CO})_2 : \text{CO}$
Alloxantin	Semiquinone of alloxan and tartronyl urea 1:1,000,000
Antipyrine	$\text{C}_6\text{H}_5 \cdot \text{C}_3\text{HON}_2 : (\text{CH}_3)_2$
8-Hydroxyquinoline (Oxine)	$\text{C}_9\text{H}_6\text{N} \cdot \text{OH}$
—5-bromo derivative	$\text{HO} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{Br}$
—5-chloro derivative	$\text{HO} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{Cl}$
—5,7-dibromo derivative	$\text{HO} \cdot \text{C}_9\text{H}_4\text{N} \cdot \text{Br}_2$
—7-iodo derivative	$\text{HO} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{I}$
—7-iodo-5-sulfonic acid derivative (Ferron)	$\text{HO} \cdot \text{C}_9\text{H}_4\text{N} \cdot (\text{I}) (\text{SO}_3\text{H})$ 1:10,000,000

#### *c. Lake-forming dyestuffs*

Alizarin	$\text{C}_6\text{H}_4 (\text{CO})_2 \text{C}_6\text{H}_2 (\text{OH})_2$
Alizarin Red S	$\text{C}_6\text{H}_4 (\text{CO})_2 \text{C}_6\text{H} (\text{OH})_2 \text{SO}_3\text{H}$
Hematin	$\text{C}_{32}\text{H}_{32}\text{O}_4\text{H}_4\text{Fe}$
Hematoxylin	$\text{C}_{16}\text{H}_{14}\text{O}_6$

#### *d. Enolizable ketones and diketones*

Acetylacetone	$\text{CH}_3\text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$ 1:17,000
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#### *e. Alpha-Dioximes*

Dimethyl glyoxime	$\text{CH}_3 \cdot \text{C} (:\text{NOH}) \cdot \text{C} (:\text{NOH}) \cdot \text{CH}_3$ 5:1,000,000
Glyoxime	$\text{CH} (:\text{NOH}) \cdot \text{CH} (:\text{NOH})$

#### *g. o-Hydroxyomines*

Resorcyldaldoxime	$(\text{OH})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} (:\text{NOH})$
Salicyldaldoxime	$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} (:\text{NOH})$



### *h. Other oximes*

Benzamideoxime	$C_6H_5.C(:NOH).NH_2$
Formaldoxime	$CH_2(:NOH)$
Cupferron	$C_6H_5N.NO.ONH_4$
Neocupferron	$C_{10}H_7.N.NO.ONH_4$

### *i. Nitroso and isonitroso compounds*

Diisonitrosoacetone	$HON:CH.CO.CH:NOH$ 1:10,000,000
2,4-Dinitrosoresorcinol	$(NO)_2.C_6H_2.(OH)_2$
Isonitrosoacetoacetic acid esters	$CH_3.CO.C(:NOH).COOR$
Isonitrosoacetone	$CH_3.CO.CH(:NOH)$
Isonitrosoacetone dicarboxylic acid esters	$ROOC.CH_2.CO.C(:NOH).COOR$
Isonitrosoacetone methyl ether	$CH_3.CO.CH:NO.CH_3$
Isonitrosoacetophenone	$C_6H_5.CO.CH:NOH$ 3:100,000,000
Isonitrosoacetylacetone	$CH_3.CO.C(:NOH).CO.CH_3$
Isonitrosobenzalacetone	$C_6H_5.CH:CH.CO.CH:NOH$
Isonitrosobenzoylacetone	$C_6H_5.CO.C(:NOH).CO.CH_3$
Isonitrosobromoacetoacetic acid esters	$CH_2Br.CO.C(:NOH).COOR$
Isonitrosocinnamalacetone	$C_6H_5.CH:CH.CH:CH.CO.$ $CH:NOH$
Isonitrosocyanacetamide	$CN.C(:NOH).CO.NH_2$
Isonitrosocyanacetylurea	$CN.C(:NOH).CO.NH.CO.NH_2$
Isonitrosodibromoacetoacetic acid esters	$CHBr_2.CO.C(:NOH).COOR$
2-Isonitroso-1-ketotetralin	$C_{10}H_8O(:NOH)$
1-Nitroso-2-naphthol	$NO.C_{10}H_6.OH$
2-Nitroso-1-naphthol-4-sulfonic acid	$NO.C_{10}H_5(OH).SO_3H$ 1:20,000,000
Nitroso-R-salt	$NO.C_{10}H_4(OH)(SO_3Na)_2$

### *k. Hydroxy-carboxylic acids*

Citric acid	$HOOC.CH(OH).CH(OH).COOH$
Protocatechuic acid	$CH_2COOH$ $(OH)_2.C_6H_3.COOH$
Beta-Resorcylic acid	$(OH)_2.C_6H_3.COOH$ 1:20,000,000
Salicylic acid	$OH.C_6H_4.COOH$ 4:10,000,000
Sulfosalicylic acid	$OH.C_6H_3(COOH).SO_3H$
Tannic acid	$C_{14}H_{10}O_9$
Tartaric acid	$HOOC.CH(OH).CH(OH).COOH$

*m. Amino-carboxylic acids*

Cysteine	$\text{HS.CH}_2\text{CH}(\text{NH}_2).\text{COOH}$
<i>o</i> -Quinaldic acid	$\text{C}_9\text{H}_6\text{N.COOH}$

*n. Arsinic and arsonic acids*

<i>p-n</i> -Butylphenylarsonic acid	$\text{C}_4\text{H}_9.\text{C}_6\text{H}_4.\text{AsO}(\text{OH})_2$
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*o. Sulfonic and sulfuric acids*

Benzensulfinic acid (?)	$\text{C}_6\text{H}_5.\text{SO}_2\text{H}$
Naphthalene-1-sulfinic acid	$\text{C}_{10}\text{H}_7.\text{SO}_2\text{H}$
Naphthalene-1-sulfinic acid	$\text{C}_{10}\text{H}_7.\text{SO}_2\text{H}$

**B. MERCAPTO GROUP**

Diethyldithiocarbamic acid (sodium salt)	$(\text{C}_2\text{H}_5)_2.\text{N.CS.SNa}$
Dithiooxalic acid (potassium salt)	$(\text{COSK})_2$
Dithiooxamide	$(\text{NH}:\text{C.SH})_2$
5-Mercapto-3-phenyl-2-thio- 1,3,4-thiodiazol-2-one	$\text{C}_6\text{H}_5.\text{N}_2\text{C}_2\text{S}:\text{S.SH}$
Thioglycolic acid	$\text{HS.CH}_2\text{COOH}$
Thiocarbonic acid	$\text{H}_2\text{CS}_3$

**C. ACTIVE IMINO GROUP**

*a. Imino group present*

<i>s</i> -Diphenylcarbazine	$(\text{C}_6\text{H}_5.\text{NH.NH})_2.\text{CO}$
Di-1-naphthylcarbazone	$\text{C}_{10}\text{H}_7.\text{NH.NH.CO.N}:\text{N.C}_{10}\text{H}_7$
Di-2-naphthylcarbazone	$\text{C}_{10}\text{H}_7.\text{NH.NH.CO.N}:\text{N.C}_{10}\text{H}_7$
<i>s</i> -Diphenylcarbazone	$\text{C}_6\text{H}_5.\text{NH.NH.CO.N}:\text{N.C}_6\text{H}_5$
Diphenylsemicarbazide	$\text{C}_6\text{H}_5.\text{NH.NH.CO.NH.C}_6\text{H}_5$

*b. Substances containing enolizable imino groups*

Alloxan	$\text{CO}:(\text{NH.CO.})_2:\text{CO}$
Alloxantin	Semiquinone of alloxan and tartronyl urea

**VIII. Basic Salinogenic Compounds**

**A. AMINES, AMIDES, AND SUBSTITUTED  
AMMONIUM COMPOUNDS**

Dibenzylamine	$\text{C}_6\text{H}_5.\text{CH}_2.\text{NH.CH}_2.\text{C}_6\text{H}_5$
1-Naphthylamine	$\text{C}_{10}\text{H}_7.\text{NH}_2$
2-Naphthylamine	$\text{C}_{10}\text{H}_7.\text{NH}_2$
<i>m</i> -Phenylenediamine	$\text{NH}_2.\text{C}_6\text{H}_4.\text{NH}_2$
Triethanolamine	$(\text{HO.C}_2\text{H}_4)_3\text{N}$

## B. NITROGEN RING COMPOUNDS

Acridine	$C_{13}H_9N$
Alloxan	$CO:(NH.CO)_2:CO$
Alloxantin	Semiquinone of alloxan and tartronyl urea
Antipyrine	$C_6H_5.C_3HON_2:(CH_3)_2$
2,2'-Dipyridyl	$C_5H_4N)_2$ 1:1,600,000
2,2'-Phenanthroline	$C_{14}H_8H_2$
2-Methyl pyridine	$C_5H_4N.CH_3$
Piperazine	$(CH_2)_4.(NH)_2$
Pyramidone	$(CH_3)_2N.(CH_3)_2.C_3N_2O.C_6H_5$ 5:100,000
Pyridine	$C_5H_5N$
2-Pyridylhydrazine	$C_5H_4N.NH.NH_2$
2-(2'-Pyridyl)-pyrrole	$C_5H_4N.C_4H_3NH$
2-(2'-Pyridyl)-quinoline	$C_5H_4N.C_9H_6N$
Quinoline	$C_9H_7N$
2-(2'-Quinolyl)-quinoline	$C_9H_6N.C_9H_6N$
2,2',2'-Tripyridyl	$(C_5H_4N)_3$

## XI. Alkaloids and Natural Products

Strychnine	$C_{21}H_{22}O_2N_2$
Sparteine	$C_{15}H_{26}N_2$
Brazilin	$C_{16}H_{14}O_5$
Citarin	$CO.OCH_2.O.C.(CH_2.COONa)_2$
Cryogenin	

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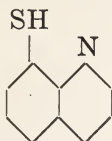
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MARY BALDWIN COLLEGE

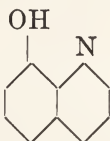
## A Note on 8-Mercaptoquinoline

J. R. TAYLOR

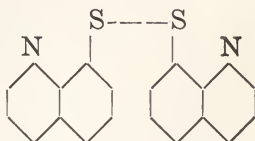
The sulfur analog (I) of 8-hydroxyquinoline (II), *oxine*, was prepared in this Laboratory for comparison of its analytical activity with that of the hydroxy compound.



(I) Mercaptoquinoline



(II) Hydroxyquinoline



(III)

(I) was prepared previously by Edinger<sup>1</sup>, who reported the formation of a double salt with stannous chloride; and by Jansen, who obtained a chelated complex ion containing divalent nickel and two moles of the mercapto compound<sup>2</sup>. The present preparation followed Edinger's method of reduction of quinoline 8-sulfonyl chloride.

The mercaptan is practically insoluble in water; soluble in alkaline solutions, and in alcohol. In solution, particularly in alkali, it is oxidized in contact with air to a non-acidic substance, which gradually precipitates. This insoluble material appears to be a disulfide (III). When run through the regular drop tests with about 78 inorganic ions, the reagent precipitated in acid solutions. In alkaline solutions, colored solids containing metal were obtained with copper(ic), silver, cobalt, nickel, platinum, and palladium. The composition of these precipitates has not been determined.

The mercaptan is not adaptable to analytical use, because of its great instability in the presence of air. There is, however, one point which may have a theoretical significance. Comparing the reactivity with that of *oxine* under comparable conditions<sup>3</sup>, it is seen that (I) reacts with fewer metals, and those which give strong tests are the metals deep in the troughs of the atomic volume curve. This may be related to the fact that scale models of the two molecules show less available space for a chelating metal with (II) than with (I).

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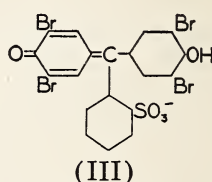
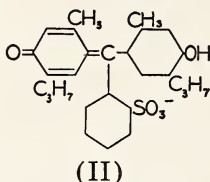
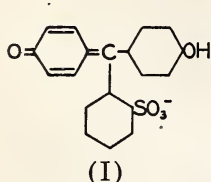
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WASHINGTON & LEE UNIVERSITY

## Some Substituted Phenolsulfonephthaleins

J. R. TAYLOR, R. S. ROSENFELD AND J. W. MARTIN, JR

The introduction of substituents into the phenolic residues of phenol red (I) causes a marked change in the value of the dissociation constant of the phenolic group. The direction of the effect is that which might be expected from the behavior of the simple substituted phenols.



The  $pK$  of phenol red is 8.0 and the color change interval, (yellow to red) is from pH 6.4 to 8.2. Introduction of alkyl groups into the phenolic rings yield weaker acids, such as thymol blue (II), with  $pK$  8.9, and change interval pH 8.0 to 9.6. Halogen, and especially the nitro group, has the opposite effect of increasing the acidity. Thus, bromphenol blue (III) has a change interval of pH 3.0 to 4.6, and the corresponding tetra-nitro compound changes between pH 2.8 and 3.8.

Substitution on the sulfobenzoic acid residue might be expected to have a much smaller effect on the indicator  $pK$ . Three compounds halogenated in this ring, prepared by Harden and Drake,<sup>2</sup> showed essentially the same color change, and through the same interval, as phenol red itself.

Since a number of substituted sulfobenzoic anhydrides and sulfobenzimides (saccharins) were available in this Laboratory from a previous investigation, it seemed to be of interest to extend the list of dyes with the purpose of testing further the effect of substitutes in the sulfobenzoic acid ring.

The method of preparation was in general that of Harden and Drake<sup>2</sup>. An excess of phenol was stirred and heated with the sulfobenzoic acid derivative and fused stannic chloride. Unreacted phenol was removed by steam distillation; the dye was leached out with soda solution, and purified by several successive precipitations. The dyes prepared were those tabulated below according to the parent sulfobenzoic acid. The amino compound was prepared by reduction of phenol aminosulfonephthalein.

Parent Anhydride	Indicator $pK$	Color change
4-Bromo-sulfobenzoic anhydride	7.8	yellow to purple
4,4-Iodo-sulfobenzoic anhydride	8.1	" "
4,6-Diiodo-sulfobenzoic anhydride	7.9	" "

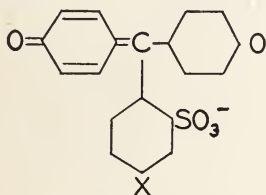


4,5,6-Tribromo-sulfobenzoic anhydride	8.0	"	"
4,5,6-Triiodo-sulfobenzoic anhydride	7.6	"	"
3-Nitro-sulfobenzoic anhydride	7.6	"	"
3-Amino-sulfobenzoic anhydride	7.9	"	"

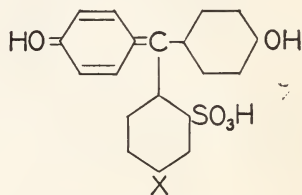
The indicator pK values were determined by comparison of paired Gillespie tubes and buffer solutions of known pH.

It is apparent that the pK values of all these compounds are practically the same as that of phenol red. In each case the change interval was approximately pH 6.5 to 8.5, the color being about the same for all the indicators. In addition, the second color change, characteristic of all the sulfonephthalein dyes in strongly acid solutions, was found to set in at about pH 1.5, the color changing from yellow to orange-red as the pH decreased.

The color of the alkaline form of the sulfonephthalein dyes is commonly attributed to the presence of a negative charge which may appear at two different points in the molecule<sup>3</sup>. In the same way, the deepening of color in strongly acid solutions may result from an oscillating positive charge. There appears to



Alkaline form



Strong acid form

be no mechanism by which the substituents in the compounds described here could affect the possible distribution of charges. It is possible that such an effect would be obtained from a derivative of 4-nitro- rather than 3-nitro-*o*-sulfobenzoic acid, so that the nature of the color change would not be the same as that of phenol red. This possibility will be tested later.

#### SUMMARY

Several new substituted sulfonephthaleins, with the substituents in the sulfobenzoic acid residue, have been prepared. Their indicator properties are essentially those of the unsubstituted phenolsulfonephthalein.

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WASHINGTON & LEE UNIVERSITY

## **Reactivities of Certain Organic Compounds with Inorganic Ions**

F. H. FISH, P. J. WALKAUSKAS AND M. FOX

Thirty organic compounds have been tested since our report was made last year. This makes a total of two hundred and eighty compounds investigated at Virginia Polytechnic Institute.

Eighteen out of the thirty compounds tested during the session 1941-1942 gave colored solutions or precipitates. The majority of these reactions, however, appear to be of little value from the standpoint of analytical chemistry. Ferric iron was the most reactive of the seventy-six inorganic ions included in the tests.

The following compounds were found to be reactive and will be investigated later:

1. 4-Ethylaminobenzoic acid gives a yellow precipitate with palladium ions and a black precipitate with silver ions.
2. p-Tolyhydrazine hydrochloride gives a black precipitate with silver ions.
3. Di-acetoacetyl 2(4'-aminophenyl) produces a deep orange precipitate with uranium ions.
4. 2,5-Diethoxy-4-acetoacetylaminophenol gives a deep yellow precipitate with cupric ions.

VIRGINIA POLYTECHNIC INSTITUTE

## **Progress Report on Inorganic Analysis with Organic Reagents**

E. LOUISE WALLACE AND ALFRED R. ARMSTRONG

Eighty organic compounds were tested by spot-plate technique during the 1941-1942 session, making a total of two hundred and fifty substances investigated at William and Mary.

Of the eighty compounds tested, thirty-nine gave color reactions and seven behaved as acid-base indicators. 1-Phenyl-3-methylpyrazoline shows some promise as a reagent for hafnium; ceric, auric, ferric, ruthenium, and chloroplatinate ions interfere.

COLLEGE OF WILLIAM AND MARY

## Organic Solvents and Wash Liquids in Analytical Chemistry

LONDON ARNDALE SARVER

Of all the manifold uses of organic substances in inorganic analysis, none are more ancient or less appreciated than the employment of liquid compounds of carbon as solvents and for the washing of vessels and precipitates.

It is not uncommon for this new-old field of knowledge to be referred to as a product of the last fifteen or twenty years. Just the other day I read an article in which it was stated that the use of organic reagents had increased steadily since the use of a carbon compound by Peter Greiss in 1879, and especially after the excellent results obtained with dimethylglyoxime in 1905. It was at least intimated by these writers that the year 1879 saw the first application of an organic compound of any kind in chemical analysis, and that the first method of any real practical value came in 1905.

Fortunately, we have here in Virginia, due to the able leadership of Professor Yoe, a group that is better informed on organic reagents than can be found in most parts of this country. Nevertheless, it may still come as a surprise to some of you that an important paper was published on the subject one hundred and eleven years ago! I make this statement from my certain knowledge, but I feel sure that still more ancient references will be found when the literature has been searched with sufficient diligence.

The foundation for the well-known perchlorate method for the determination of potassium was laid by Sérullas in 1831, when he discovered that potassium perchlorate is a great deal more soluble in ethanol than are the perchlorates of sodium and lithium. Even today, this is still one of the very best methods for the separation of the alkalis.

As a matter of fact, publications on organic reagents have been fairly regular since 1856; at least one paper has been published every twelve months for the past seventy-one years; and there have been not less than seven annually for the past half-century. Investigators had already been active for three-quarters of a century when the analytical value of dimethylglyoxime for the determination of nickel was first disclosed to the world.

Personally, I think that 1-nitroso-2-naphthol has been very valuable for the separation of cobalt from nickel in acid solution, and the first work on this was published in 1885. In recent years, both Dr. Yoe and myself have been active in investigating the behavior of some derivatives of 1-nitroso-2-naphthol as colorimetric reagents for cobalt.

While the bulk of the earlier researches on organic analytical

reagents were concerned chiefly with colorimetric qualitative tests for various ions, particularly nitrates and nitrites, it just happens that several of the very oldest had to do with solvents. The use of ethanol in the perchlorate method for potassium has already been mentioned. Struve, in 1869, discovered that traces of iodine could be detected by extracting it from aqueous solution with carbon disulfide; iodides and iodates could also be detected by first liberating the iodine and then extracting it. And Kersting, in 1863, tested potable waters for nitrates by means of an alcoholic solution of brucine.

## SOLVENT FUNCTIONS OF ORGANIC LIQUIDS

Organic liquids may be used as solvents for a variety of purposes, among which are the following:

TABLE I

### SOLVENT FUNCTIONS OF ORGANIC LIQUIDS

I. WASHING	IV. CHANGE IN IONIC ACTIVITIES
[a] Vessels	[a] Differential crystallization
[b] Precipitates	[b] Control of dissociation
[c] Other liquids	[c] Intensification of colors
[d] Gases	
II. DRYING	V. MISCELLANEOUS USES
[a] Vessels	[a] Solvents for reagents
[b] Precipitates	[b] Protective layers
[c] Other liquids	[c] Control of foaming
[d] Gases	[d] Collection of precipitates at interface
III. EXTRACTIONS	[e] Aids to distillation
[a] Liquid-solid	[f] Reducing post-precipitation
[b] Liquid-liquid	
[c] Liquid-gas	

I. WASHING. The washing of [a] laboratory vessels, and [b] quantitative or qualitative precipitates are probably the oldest uses for organic liquids in analytical chemistry; and only a careful perusal of the early literature would reveal the first application of this kind. In addition to this, they are also frequently employed for washing other liquids and solutions [c] with which they are immiscible, and [d] for the scrubbing of gases and vapors.

II. DRYING. Some organic solvents are miscible with water, and possess at the same time a high vapor pressure at ordinary temperatures, while in other cases a substance of low vapor



pressure is mutually miscible with water and another liquid of high vapor pressure. Acetone, for example, can be used for the drying of [a] pipets and other vessels, and [b] of precipitates; but the same result can also be accomplished by rinsing first with alcohol, and then with ether. Further, as was the case with washing, organic liquids can be used for the drying of [c] other liquids, or [d] for the drying of gases.

III. EXTRACTION. The first recorded use of an organic solvent of which we are at present aware was [a] a liquid-solid extraction; Sérullas found in 1831 that if the dehydrated mixture of sodium and potassium perchlorates be treated with ethanol, the sodium salt dissolves, and potassium perchlorate can be filtered off. The third recorded use of an organic analytical reagent was [b] of a liquid-liquid extraction; for Struve, in 1869, extracted traces of iodine from aqueous solution, and concentrated it in a small volume of carbon disulfide so as to intensify its color. Organic liquids may equally be employed [c] to absorb some constituent from a gaseous mixture.

IV. CHANGE IN IONIC ACTIVITIES. The addition of organic liquids to aqueous solutions often brings about profound changes in the properties of such solutions. The use of ethanol for decreasing the solubility [a] of lead sulfate in water or dilute sulfuric acid is well-known. Acetone [b] has been employed extensively for intensifying the blue color in the thiocyanate test for cobalt; it does this, of course, by shifting the equilibrium in favor of the undissociated cobalt thiocyanate. The same general effect can also be accomplished in the case of colorless substances [c], whenever it is desired to eliminate the interference of some ion with an analytical reaction.

V. MISCELLANEOUS USES. The second recorded application of organic substances in analytical chemistry was [a] as a solvent for an added reagent, when Kersting, in 1863, detected nitrates in drinking water by means of an alcoholic solution of brucine. Liquids that are immiscible with water [b] can be used as protective layers to eliminate the effects of oxygen or carbon dioxide in the air. Substances such as octyl alcohol [c] can be employed for the control of foaming. Liquids that are immiscible with water, such as benzene or ether, can serve [d] for the collection of very small precipitates at the interface. Liquids that are immiscible with water, like toluene or heptane, are employed regularly as aids to distillation [e] in the determination of moisture. And certain unsaturated aldehydes, notably acrolein and crotonaldehyde, have proven themselves invaluable in [f] reducing the post-precipitation of zinc sulfide along with cupric sulfide.

#### FACTORS AFFECTING THE CHOICE OF SOLVENT

A number of factors have to be considered in choosing a solvent for a given purpose.



TABLE II

## FACTORS AFFECTING THE CHOICE OF SOLVENT

- |                            |                         |
|----------------------------|-------------------------|
| 1. Suitability for purpose | 7. Vapor pressure       |
| 2. Cost                    | 8. Boiling point        |
| 3. Toxicity and odor       | 9. Freezing point       |
| 4. Flammability            | 10. Surface tension     |
| 5. Specific gravity        | 11. Refractive index    |
| 6. Viscosity               | 12. Dielectric constant |

[1] The primary consideration is in all cases the general suitability of the liquid for the work that has to be done. This in turn is dependent upon a number of other properties.

[2] Cost and availability have to be borne in mind; for it is useless to select a solvent that is so difficult to manufacture as to be either unavailable in quantity or so expensive that its cost is prohibitive.

[3] A solvent should preferably be odorless and non-toxic, although this is an ideal rather difficult to obtain. The great majority of organic liquids are afflicted with some degree of toxicity, and many of them have odors that are far from pleasant. However, other qualities may frequently out-weigh these handicaps, and toxic substances may be employed with proper provisions for safety.

[4] It is most important that a solvent shall not be too easily inflammable, but this danger can be overcome also by proper attention to safety.

[5] The specific gravity affects the choice of solvent most when it is to be used in liquid-liquid extractions. Obviously, its density must be appreciably different from that of the solution to be extracted; whether it should be greater or less depends upon whether it is most convenient to have the organic layer on the top or on the bottom.

[6] The vapor pressure should be high if the solvent is to be used for drying, or if it will be necessary to evaporate it off later; on the other hand, the vapor pressure should be low if undue loss of solvent must be prevented.

[7] The boiling point is closely bound up with vapor pressure, and the same considerations apply.

[8] The freezing point should in general not be too high, lest the liquid solidify at temperatures at which it is necessary to work.

[9] The viscosity should be reasonably low, because extremely viscous liquids may be very troublesome.

[10] Some organic liquids lower the surface tension of solutions to such an extent that serious difficulties are encountered with foaming; hence, the lowering of surface tension should not be unduly great.

[11] The refractive index is sometimes of interest, especially in microscopic work.

[12] The dielectric constant might be important in some cases, although I do not recall any one in which this is true.

#### TYPES OF ORGANIC LIQUIDS THAT MAY BE USED AS SOLVENTS

There are more than a hundred organic liquids that are available commercially, and might be used as solvents. It would neither be interesting nor of any particular value to mention all of these today. However, they can be classified into a small number of groups.

TABLE III

#### TYPES OF ORGANIC LIQUIDS

- |                           |                         |
|---------------------------|-------------------------|
| I. HYDROCARBONS           | VI. ALDEHYDES           |
| A. Aliphatic Hydrocarbons | A. Acyclic Aldehydes    |
| B. Aromatic Hydrocarbons  | B. Cyclic Aldehydes     |
| II. SUBSTITUTED           | VII. KETONES            |
| HYDROCARBONS              | A. Acyclic Ketones      |
| A. Sulfur Derivatives     | B. Cyclic Ketones       |
| B. Chlorine Derivatives   | VIII. ESTERS            |
| III. ALCOHOLS             | A. Organic Esters       |
| A. Monohydric Alcohols    | B. Inorganic Esters     |
| B. Polyhydric Alcohols    | IX. NITROGENOUS         |
| IV. ALCOHOL ETHERS        | COMPOUNDS               |
| A. Cellosolves            | A. Substituted Ammonias |
| B. Carbitols              | B. Heterocyclic Bases   |
| V. ETHERS                 | X. ACIDIC COMPOUNDS     |
| A. Simple Ethers          | A. Organic Acids        |
| B. Chlorinated Ethers     | B. Acid Anhydrides      |

- I. HYDROCARBONS. A. Aliphatic hydrocarbons [e.g., hexane].  
 B. Aromatic hydrocarbons [e.g., benzene, toluene, xylene].

- II. SUBSTITUTED HYDROCARBONS. A. Sulfur derivatives [e.g., carbon disulfide].

- III. ALCOHOLS. A. Monohydric alcohols [e.g., methanol, ethanol, 2-propanol, butyl alcohols, amyl alcohol, octyl alcohol, cyclohexanol].

- B. Polyhydric alcohols [e.g., ethylene glycol, glycerol].

- IV. ALCOHOL ETHERS AND THEIR ESTERS. A. The "cellosolve" solvents [e.g., ethylene glycol monomethyl ether [methyl cellosolve], ethylene glycol monoethyl ether [cellosolve], ethylene glycol mono-n-butyl ether [butyl cellosolve], ethylene glycol monoethyl ether acetate [cellosolve acetate]].

B. The "carbitol" solvents [e.g., diethylene glycol monomethyl ether [methyl carbitol], diethylene glycol monoethyl ether [carbitol], diethylene glycol mono-n-butyl ether [butyl carbitol], diethylene glycol monoethyl ether acetate [carbitol acetate]].

V. ETHERS. A. Simple ethers [e.g., ether, isopropyl ether, n-butyl ether].

B. Chlorinated ethers [e.g., dichloroethyl ether, dichloroisopropyl ether].

VI. ALDEHYDES. A. Acyclic aldehydes [e.g., n-hexaldehyde].

B. Cyclic aldehydes [e.g., furfural].

VII. KETONES. A. Acyclic ketone [e.g., acetone, 2-butanone].

B. Cyclic ketones [e.g., cyclohexanone, isophorone]

VIII. ESTERS. A. Esters of organic acids [e.g., ethyl acetate, methyl acetate].

B. Esters of inorganic acids [e.g., diethyl carbonate, triethyl borate, tri-n-butyl borate, ethyl nitrate, diethyl sulfate].

IX. NITROGENOUS COMPOUNDS. A. Substituted ammonias [e.g., diethylamine, dipropylamine, dibutylamine, tetraethylenepentamine [possibly for the determination of free sulfur]].

B. Heterocyclic bases [e.g., pyridine, quinoline, morpholine].

X. ACIDIC COMPOUNDS. A. Organic acids [e.g., acetic acid, propionic acid].

B. Acid anhydrides [e.g., acetic anhydride, propionic anhydride].

## OUTSTANDING APPLICATIONS OF ORGANIC SOLVENTS

1. Use of ethanol in the perchlorate and chloroplatinate methods for the separation of the alkalis.

2. Use of ethanol for the intensification of the color in the thiocyanate test for cobalt.

3. Use of chloroform for extracting and intensifying the colors in "dithizone" tests for heavy metals.

4. Use of ether for extracting and removing large quantities of ferric chloride in iron and steel analysis; higher boiling ethers may be substituted advantageously.

5. Use of carbon disulfide for dissolving crystalline sulfur.

6. Use of hydrocarbons in moisture determinations.

7. Use of "methyl cellosolve" as reaction medium in the thiocyanate colorimetric method for ferric iron, and in the diethyldithiocarbamate colorimetric method for carbon disulfide.

8. Substitution of isopropyl alcohol for ethanol in many cases, because of lower cost.

## DETERMINATION OF XANTHATE SULFUR IN VISCOSE SOLUTIONS

It often happens that natural products are so complex that it is extremely difficult to assign to them an exact structural formula, and so it is with cellulose. We know that it is a so-called carbohydrate, containing carbon, hydrogen and oxygen in the proportions represented by the formula  $C_6H_{10}O_5$ ; but we also know that it is not as simple as this, but has a very large molecular weight. It is, therefore, a polymer of the simple unit just mentioned, and can be written  $[C_6H_{10}O_5]^n$ . It is fairly certain that natural cellulose is made up of long chains built up from the basic units, and these chains may be of varying lengths. Furthermore, the molecules possess active hydroxyl groups which readily exchange hydrogen for sodium atoms when treated with caustic alkali; and this alkali cellulose reacts in turn with carbon disulfide to yield a water-soluble sodium cellulose xanthate. The cellulose xanthate micelles swell, imbibe water, and become dispersed in colloidal solution. After preparation of the viscose solution, complex changes immediately set in, accompanied by profound changes in the composition, viscosity, and spinning properties of the solution. By hydrolysis, or simple decomposition, or both, the concentration of xanthate sulfur continuously decreases, while that in the form of sulfides or thiocarbonates continuously increases. And as the concentration of electrolytes increases, the cellulose or cellulose xanthate micelles lose water through their semi-permeable walls, and become more and more easily coagulable, until finally the solution sets to a gel. The relative concentration of xanthate and by-product sulfur are, therefore, of considerable importance in the control of spinning operations.

A number of more or less ingenious analytical methods have been proposed for making these determinations, but the most reliable ones generally involve determining sulfur by conventional gravimetric methods in the whole solution and in the filtrate obtained after coagulating and filtering off the xanthate; the xanthate sulfur is then found by difference. This procedure is not only tedious but also subject to the criticism that further changes are likely to occur while the analysis is in progress. Therefore, I have developed a new method which I think combines both speed and accuracy.

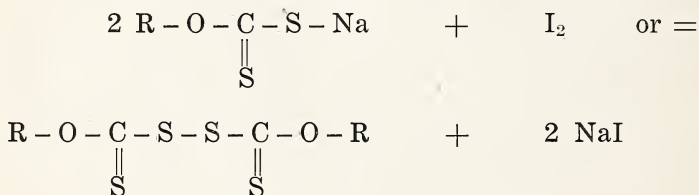
First, I speeded up enormously the dispensing of the sample by means of a novel piston pipet [exhibited]. Similar pipets have been described before, but I think that mine is a better one. A large hypodermic syringe is fitted with a special monel head, so that positive deliveries can be made with extreme accuracy [errors being of the order of 1 part in 10,000]. The



sample is sucked into the syringe, and any bubbles eliminated by inversion. The piston is depressed until the stud hits a marked spot on the flange, after which the tip is wiped clean. The sample is then delivered quickly by rotating the piston until the stud clears the flange, and pushing all the way down. Even with the extremely viscous viscose solutions, samples can be measured in less than a minute with as great an accuracy as could be obtained by weighing.

A few milliliters of iced distilled water are first mixed with the measured samples to thin them a little, and the xanthate is then coagulated quickly with ethanol. The liquid is sucked off quickly through Gooch crucibles, and the white precipitates are washed thoroughly with ethanol. They are then redissolved at once with dilute alkali, treated with a measured excess of potassium iodate, acidified with acetic acid, and the excess of liberated iodine determined by means of sodium thio-sulfate solution.

The pure cellulose xanthate is easily oxidized to a dixanthate, with the consumption of one atom of iodine for each xanthate group [containing two sulfur atoms]. A whole series of determinations can be run in less than an hour, and the results agree well with those obtained by conventional gravimetric methods. The oxidation of an alkali xanthate is illustrated by the following equation:



I have described this new application of an organic solvent to industrial analysis, in order to illustrate the general principle that old and well-known reagents can be frequently employed in novel and useful methods. It is equally true that one should always seek for new and better reagents, wherever they can be applied in old and conventional methods.

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## *anti*-Dianisalacetoneoximehydroxylamine as a New Organic Reagent for the Gravimetric Determination of Tungstates

A. LETCHER JONES AND JOHN H. YOE

The two isomers, *syn*- and *anti*- dianisalacetoneoximehydroxylamine, have been prepared. The *syn* isomer is a white crystalline substance, sparingly soluble in ethyl alcohol, melts at 217°-220°C. and is unreactive with tungstates. The *anti* isomer is a yellow crystalline substance quite soluble in ethyl alcohol, melts at 157°C., and reacts with tungstates in aqueous acid medium to form a heavy, deep yellow colored, highly insoluble flocculent precipitate.

Analysis of the organic tungsten complex, formed by the reaction of the *anti* isomer with tungstates, showed that the organic molecule combines with the  $\text{WO}_4$  ion in a ratio of one to one.

An extensive investigation of this reagent is now in progress and the procedures for the use of it in the analyses of tungsten ores and alloys are being developed.

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## Sodium Catechol Disulfonate as a New Colorimetric Reagent for Iron

A. LETCHER JONES AND JOHN H. YOE

Sodium catechol disulfonate combines with ferric iron to form a highly colored and extremely stable complex. Below a pH value of 5 the complex is blue; above 7 it is deep red in color. By means of the red complex one part of iron in 200 million parts of solution may be detected; the blue complex is somewhat less sensitive enabling detection of approximately one part of iron in 30 millions.

Spectrophotometric studies of the color change with changing pH have been made. The wavelengths at which the maximum absorbancy shifts have likewise been determined.

The colored complexes do not fade on standing, even after periods of many months. The reagent seems to be ideally suited for the colorimetric determination of ferric iron and a thorough investigation of it is now under way.

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## Spectrophotometric Studies of Some Complex Copper Compounds

JAMES W. COLE, M. BROOKS SHREAVES AND JAMES E. BOWDEN

Many water soluble amines upon addition to aqueous solutions of copper salts cause a deepening of the blue color of the original solution. This color change to deep blue or violet has been widely used as a colorimetric test for the cupric ion (1). Many compounds of a complex nature have been isolated from these colored solutions and their empirical formulas determined. Werner (2) in his classical coordination theory, pointed out that there is a definite spatial arrangement of groups about a central ion in the cases of complex compounds involving ammonia and halogenides. With the advent of the electronic theory of valence, considerable light was shed on possible mechanisms for the formation of complexes involving ammonia or organic amines (3). The assumption that amine nitrogen acts as a donor of electrons to form stable complex structures has been a valuable hypothesis in choosing organic analytical reagents.

The spectrophotometer has been used for some time to determine small concentrations of ions from the colors they produce with salinogenic (salt-forming) reagents. This instrument has been extremely valuable in showing conformity to, and anomalies in, Beer's law (4). More recently (5a,b,c,d) the spectrophotometer has proven of much value in elucidating the structure of complex ions in aqueous solutions. It is with the latter application that this paper is particularly concerned.

In this work we employed a Beckman Quartz Spectrophotometer, Model D, and have extended the methods of Vosburgh and Cooper (5a), and Bent and French (5c) to a series of solutions containing a sequence of mol ratios of copper sulfate to mono-, di-, and tri-ethanolamines. A wave length range from 350 to 2000 milimicrons was used. The results indicate the existence of complex ions of the general formula,  $\text{Cu}[\text{N}(\text{C}_2\text{H}_4\text{OH})_n]^{+n+}$ , where  $n$  equals 1, 2 and 3. The characteristic blue color appears to be due largely to ions with the higher values of  $n$ . This is not conclusive, however, since the addition of a strong base, such as KOH, to a solution containing the complex ions, causes a shift in the position of the maximum wavelength, as well as an increase in optical density. This effect cannot be attributed to repression of ionization of the amine base, but rather appears to be associated with a coordination of  $\text{OH}^-$  ion with the metallic ion. Additional study is needed to clear this question. Incidentally, the addition of a strong base to a solution containing  $\text{Cu}^{++}$  and triethanolamine is a more sensitive indicator for  $\text{Cu}^{++}$  than is triethanolamine alone (4).

Spectrophotometric studies of aqueous solutions made from

pure copper ethanolamine salts of known composition (6), confirm the conclusions drawn from the study of aqueous solutions of copper sulfate and the ethanolamines. The general structure of these complex ions appears to involve polydentate linkages between the central  $\text{Cu}^{++}$  and the functional groups of the ethanolamines. It would seem that cupric ion when forming complex ions with amines has a coordination number of 6 and that when  $n=1$ , the number of additional groups needed to satisfy the coordination number comes from the solvent.

A spectrophotometric investigation was also made of the copper ammonia system in aqueous media over the wavelength range 350-2000 millimicrons. The results were treated by the methods of Vosburgh and Cooper (5a), and Bent and French (5c). Our data were not in complete agreement with those of Vosburgh and Cooper. These investigators reported the existence of only  $\text{Cu}(\text{NH}_3)_2^{++}$  and  $\text{Cu}(\text{NH}_3)_4^{++}$ , but our results indicate the possibility of a series of complex ions having the general formula,  $\text{Cu}(\text{NH}_3)_x(\text{H}_2\text{O})_y^{++}$ , where  $x$  has values from 1 to 6 and  $y = 6-x$ , for each value of  $x$ .

In conclusion, it would seem that cupric ion in dilute aqueous medium has its coordination number of 6 satisfied by solvation until a compound containing amine nitrogen is added to the solution. When this happens, there is a displacement of water molecules from the sphere of influence of the ion with subsequent replacement by amine nitrogen. In the case of two functional groups in the same molecule, as with monoethanolamine, the groups being  $\text{NH}_2$  and  $\text{OH}$ , there appears to be an additional stabilizing factor in the complex ion because of the bidentate linkage.

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**Organic Analytical Reagent Studies:  
New Colorimetric Reagents for Silver, Copper,  
Cobalt, Zirconium, and Phenothiazine**

JOHN H. YOE AND LYLE G. OVERHOLSER

In an extensive search for specific and highly sensitive reagents, five new colorimetric reactions have been discovered and these reactions have been made the basis for the colorimetric detection or determination of silver, copper, cobalt, zirconium, and phenothiazine, respectively.

*Silver.* 2-Thio-5-keto-4-carbethoxy-1,5-dihydropyrimidine forms a purple colored compound with silver ions. The reaction is sensitive to about 1 part of silver in 30,000,000 parts of solution at the lowest concentration, but will detect 1 part in 100,000,000 by working in the most sensitive range. A colorimetric method for the detection and determination of silver has been developed and a critical study has been made of various factors, including reaction rate, stability, interference, sensitivity, temperature, and hydrogen ion concentration. Relative absorption curves for the reagent and for the colored silver compound have been obtained. For a full report, see Ind. Eng. Chem., Anal. Ed., 14, 148 (1942). A method of synthesis of the reagent is given by Yoe and Boyd in the J. Am. Chem. Soc., 64, 1511 (1942).

*Copper.* 2,4-Diacetoxybenzonitrile reacts with copper in weakly ammoniacal medium to give an unstable purple color which changes to a stable yellow-orange color on standing. It is possible to detect copper at a concentration of 1 part in 50,000,000 if the solution is allowed to stand overnight; at a concentration of 1 part in 10,000,000 a pronounced color develops in several hours. The slow reaction rate, sensitiveness to pH changes and the influence of a number of ions on the color formation greatly reduces the value of the reagent for colorimetric analysis. The reaction is interesting from a theoretical standpoint due to the catalytic action of traces of copper on the reaction with several other ions.

*Cobalt.* Nitrosoresorcinol reacts with cobalt to give a deep red colored complex, solutions of which may be used for the colorimetric detection and determination of small amounts of cobalt. Both visual and spectrophotometric studies have been made. Optimum conditions for the use of this reagent have been established and the effect of pH and salt concentration, reaction rate, stability, sensitivity, and interference of other ions have been determined. Procedures for the determination of cobalt in the presence of iron and nickel have been developed.

*Zirconium.* Studies with a number of substituted bromamine



acids have shown that they react with tri- and tetravalent cations in aqueous medium giving red precipitates. In acid solution, the reactivity is limited to only a few of the ions, of which the reaction with zirconium is the most sensitive. 5-Chlorobromamine acid (the sodium salt of 1-amino-4-bromo-5-chloro-2-anthraquinonesulfonic acid) was found to be the most selective of the compounds studied. The reagent is not suitable as a quantitative precipitant for zirconium but may be used for its detection, being sensitive to 1 part in 500,000 parts of solution. The interference of foreign ions has been determined and the optimum conditions for the use of the reagent have been established. See Ind. Eng. Chem., Anal. Ed., 15, 73 (1942) for further details.

*Phenothiazine.* Observation of the reactions of phenothiazine revealed that it reacts with a number of inorganic ions. Most of these ions are oxidizing agents and the red or green colored solutions formed are due to the oxidation of phenothiazine. Palladous chloride, however, reacts with phenothiazine yielding a dark blue colored solution or precipitate which is not an oxidation product but a complex having the formula  $\text{Pd}(\text{C}_{12}\text{H}_9\text{NS})_2\text{Cl}_2$ . A procedure has been developed for the colorimetric determination of small amounts of phenothiazine based on this reaction. The complex has been isolated and its properties studied. A full report will be found in Ind. Eng. Chem., Anal. Ed., 14, 646 (1942).

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## Reactivity of Substituted Thioureas

LYLE G. OVERHOLSER AND JOHN H. YOE

The examination of the reactions of 60 substituted thioureas with inorganic ions was undertaken to ascertain whether or not any of the reactions might be more sensitive than those given by thiourea, especially with bismuth.

The substituted thioureas give reactions similar to those of thiourea and although a number are as sensitive, or even slightly more sensitive, they offer no advantage to justify their use in place of thiourea. No correlation of the reactivity or non-reactivity of certain ions with the structure of the substituted thioureas was possible because of the similarity of the reactions. The difference in solubility of the compounds appeared to play a more important part in their reactivity than did the presence of any particular group. Similarly, no correlation of sensitivity and structure was noted. Further details may be found in *Ind. Eng. Chem., Anal. Ed.*, 14, 435 (1942).

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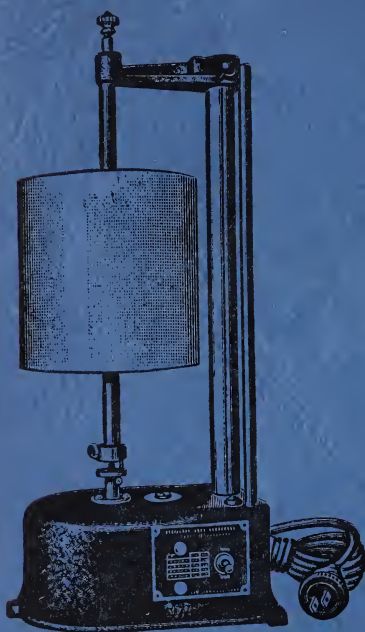
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